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### (54) RECORDING SHEETS AND PROCESS FOR THE PRODUCTION THEREOF

AUFZEICHNUNGSSCHICHTEN UND VERFAHREN ZU DEREN HERSTELLUNG

FEUILLES D'IMPRESSION ET LEUR PROCEDE DE PRODUCTION

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## Description

[0001] The present invention relates to a recording sheet and a method for its manufacture and more particularly to a recording sheet which is excellent in ink absorption and water-resistance and, hence, of use in an ink jet recording system and a method for its manufacture.

[0002] The ink jet recording system is rapidly prevailing these days, because the system is well adaptable to full-color image reproduction, less noisy, and superior in the quality of prints. From the standpoint of safety and recordability, water-based inks are mostly employed for ink jet recording in which droplets of an ink are ejected from a nozzle against a recording sheet for image recording. Therefore, the recording sheet is required to absorb the ink quickly. Thus, when a recording sheet of low ink absorption is used, the ink remains long on the surface of the recording sheet after completion of recording so that the record is easily smeared on contact with the equipment, with the operator, or with recorded sheets piled on one another. Moreover, in the high-density image area, the ink supplied in a large quantity is not well absorbed but flows out to cause a blurred image.

[0003] JP-A-57-36692 discloses an ink jet recording sheet coated with a basic latex polymer for improved water resistance and better image resolution. It is mentioned in this literature that a water-soluble polymer and a pigment, among others, can be incorporated. JP-A-63-115780 discloses an ink jet recording sheet comprising a support and a coating layer composed of a quaternary ammonium salt-containing polymer and teaches the concomitant use of synthetic silica and, as a binder, polyvinyl alcohol or the like. JP-A-7-61113 discloses an ink jet recording medium having an ink receiving layer composed of a polyvinylacetal resin and a cationic compound. JP-A-6-227114 discloses an ink jet recording sheet having an ink receiving layer composed of a pigment, such as microfine silica powder and an amphiphilic or zwitterion latex.

[0004] In these recording sheets, ink fixation and water resistance have been improved in certain degrees. However, a conflicting relation holds between ink fixation/water resistance and ink absorption. Namely, any improvement in water resistance is inevitably accompanied by a decrease in ink absorption. Thus, high water resistance and high ink absorption can hardly be reconciled at the same time.

[0005] JP-A-1-174484 discloses an ink jet recording sheet comprising a substrate sheet and, as disposed thereon, a coating layer comprising a pigment and a copolymer of a fatty acid vinyl ester, e.g. vinyl acetate, with a cationic monomer. This literature also teaches that the cationic copolymer may be a copolymer containing a nonionic monomer unit or a polyvinyl alcohol graft copolymer, and may further contain a water-soluble polymer binder. JP-A-62-83178 proposes an ink jet recording sheet having a coating layer comprising finely divided silicic acid and a cationic polymer emulsion. This literature further mentions that it is preferable to use a self-crosslinkable acrylic emulsion having a glass transition temperature of not higher than 0°C as an adhesive.

[0006] These recording sheets feature improved water resistance. However, the attained water resistance is not high enough so that when the sheet comes into contact with waterdrops, for instance, the character or picture image bleeds out and, in extreme cases, disappears locally to drastically reduce the quality of the record. Thus, it is difficult to improve water resistance and ink absorption in sufficient measures while insuring an improved quality of the print at the same time.

[0007] JP-A-6502358 discloses an article comprising a substrate bearing on at least one major surface thereof a hydrophilic liquid absorbent, semi-interpenetrating network formed from a polymer blend comprising at least one crosslinkable polymer and at least one liquid-absorbent polymer comprising a water-absorbent polymer. The blend is provided in the form of a solution being applied on the substrate. Crosslinking is either carried out with polymers with tertiary amino groups and an alkylating agent, the amino groups becoming cationic thereby, or using polymers with silanol groups via removal of water.

[0008] It is, therefore, the object of the present invention to provide a recording sheet greatly improved in both water resistance and ink absorption and a method of producing the recording sheet, and further to provide a recording sheet by which the two conflicting characteristics of water resistance and ink absorption are reconciled with each other and a method of producing the same sheet.

[0009] This object is achieved by a recording sheet comprising a substrate and an ink absorbing layer formed on at least one side of the substrate, wherein said ink absorbing layer is obtainable from a coating composition comprising:

- an aqueous cationic polymer emulsion having a surface potential ( $\zeta$  potential) of 10 to 60 mV, wherein the cationic polymer is a copolymer of monomers comprising either

(1) a cationic monomer having tertiary amine salt groups or quaternary ammonium salt groups and a crosslinking monomer having an alkoxysilyl group, or

(2) a cationic monomer having tertiary amine salt groups or quaternary ammonium salt groups, a crosslinking monomer having an alkoxysilyl group, and a hydrophilic monomer, and

- a hydrophilic polymer.

**[0010]** This object is also achieved by a method of manufacturing a recording sheet which comprises forming an ink absorbing layer on at least one side of a substrate wherein said ink absorbing layer has the composition of the ink absorbing layer according to any of claims 1-13, and further by a composition for forming an ink absorbing layer of a recording sheet, which comprises:

- an aqueous cationic polymer emulsion having a surface potential ( $\zeta$  potential) of 10 to 60 mV, wherein the cationic polymer is a copolymer of monomers comprising either :

(1) a cationic monomer having tertiary amine salt groups or quaternary ammonium salt groups and a crosslinking monomer having an alkoxysilyl group, or

(2) a cationic monomer having tertiary amine salt groups or quaternary ammonium salt groups, a crosslinking monomer having an alkoxysilyl group, and a hydrophilic monomer; and

- a hydrophilic polymer.

**[0011]** The combined use of a cationic polymer having at least crosslinking or crosslinkable groups and a hydrophilic polymer (macromolecular compound) results in improvements in water resistance and ink absorption and the combined use of a cationic polymer and a hydrophilic polymer (macromolecular compound) which are mutually reactive leads to still greater improvements in both water resistance and ink absorption.

**[0012]** The recording sheet according to the present invention, therefore, comprises a substrate (support sheet) and, as disposed on at least one side thereof, an ink absorbing layer made of a cationic polymer as defined in present claim 1 and having crosslinking or crosslinkable groups and a hydrophilic polymer (macromolecular compound). In this recording sheet, the cationic polymer may comprise an acrylic polymer emulsion as defined in present claim 2. The cationic polymer comprises either (1) or (2) as defined in present claim 1. The crosslinking monomer has hydrolyzable condensing (hydrolytically condensing) alkoxysilyl groups. The hydrophilic monomer may have a polyoxyalkylene unit. The recording sheet of the present invention is a recording sheet comprising a substrate (support sheet) and, as disposed on at least one side thereof, an ink absorbing layer as defined in present claim 1.

**[0013]** The present invention is further directed to a method of producing a recording sheet according to present claim 14.

**[0014]** The term "hydrophilic polymer" is used in this specification to mean any of various high molecular weight substances (macromolecular compounds) having an affinity for water, thus including water-absorbing polymers and water-soluble polymers.

**[0015]** The recording sheet of the present invention comprises a substrate or support and an ink absorbing layer, and the ink absorbing layer comprises at least a cationic polymer as defined in present claim 1 having crosslinking or crosslinkable groups. This recording sheet is of great value as a recording sheet for ink jet recording in which flying droplets of ink are used to form a record.

[Substrate]

**[0016]** The substrate may be opaque, translucent, or transparent depending on the intended application. For the use as an overhead projector (OHP), the substrate is usually transparent.

**[0017]** There is no particular limitation on the kind of substrate. Thus, the substrate or support includes but is not limited to paper, coated paper, nonwoven cloth, and plastic film. Plastic film is preferred among these substrates.

**[0018]** As the polymers for constituting the plastic film, there may be mentioned polyolefins such as polyethylene and polypropylene, ethylene-vinyl acetate copolymer, polyvinyl chloride, vinyl chloride-vinyl acetate copolymer, poly(meth)acrylic acid esters, polystyrene, polyvinyl alcohol, ethylene-vinyl alcohol copolymer, cellulose derivatives such as cellulose acetate, polyesters (e.g. polyalkylene terephthalates such as polyethylene terephthalate and polybutylene terephthalate, polyalkylene naphthalates such as polyethylene naphthalate and polybutylene naphthalate), polycarbonates, polyamides (e.g. polyamide 6, polyamide 6/6, polyamide 6/10, polyamide 6/12), polyesteramides, polyethers, polyimides, polyamideimides, and polyetheresters. Furthermore, the corresponding copolymers, blends, and crosslinked polymers can be employed.

**[0019]** Among the above-mentioned films, polyolefin (particularly polypropylene), polyester (particularly polyethylene terephthalate, etc.), and polyamide films are generally employed. From the standpoint of mechanical strength and processability, polyesters (particularly polyethylene terephthalate) are preferred.

**[0020]** The thickness of the support can be liberally selected according to the intended application, and is generally 5 to 250  $\mu\text{m}$  and preferably 10 to 200  $\mu\text{m}$ . The thickness of the film for OHP use may, for example, be 50 to 200  $\mu\text{m}$ .

[0021] Where necessary, the conventional additives such as antioxidants, ultraviolet absorbers, heat stabilizers, lubricants, pigments, etc. can be incorporated in the plastic film. Moreover, the film may be subjected to a surface treatment such as corona discharge treatment or undercoat treatment, for enhanced adhesion to the ink absorbing layer.

[Ink absorbing layer]

[0022] The ink absorbing layer is formed from a cationic polymer and a hydrophilic polymer according to present claim 1. The ink absorbing layer of the recording sheet according to the present invention is constructed by using a cationic polymer (1) or (2) according to present claim 1, and a hydrophilic polymer.

[0023] The cationic polymer mentioned above has at least crosslinking groups. The crosslinking group-containing cationic polymer is (1) or (2). The preferred cationic polymer comprises the above-mentioned polymer (2).

[0024] The cationic monomer includes not only a variety of monomers each having a tertiary amino group or a salt thereof, but also a variety of monomers each having, a quaternary ammonium salt.

[0025] The cationic monomer thus includes, for example, di- $C_{1-4}$  alkylamino- $C_{2-3}$  alkyl(meth)acrylamide salts [dimethylaminoethyl(meth)acrylamide, diethylaminoethyl(meth)acrylamide, dimethylaminopropyl(meth)acrylamide, diethylaminopropyl(meth)acrylamide salts], di- $C_{1-4}$  alkylamino- $C_{2-3}$  alkyl (meth)acrylate salts [(dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)acrylate, diethylaminopropyl (meth)acrylate salts], salts of di- $C_{1-4}$  alkylamino- $C_{2-3}$  alkyl-substituted aromatic vinyl compounds [4-(2-dimethylaminoethyl)styrene, 4-(2-dimethylaminopropyl)-styrene], and nitrogen-containing heterocyclic monomers [vinylpyridine, vinylimidazole, vinylpyrrolidone salts]. The salts mentioned above include salts with hydrohalogenic acid (hydrochloride, hydrobromide), sulfates, alkylsulfates (methylsulfate, ethylsulfate), alkylsulfonates, arylsulfonates, and carboxylates (acetate). It should be understood that an alkylating agent (epichlorohydrin, methyl chloride, benzyl chloride) can be permitted to act upon the tertiary amino group to form a quaternary ammonium salt.

[0026] The crosslinking monomer includes silyl condensing group-containing monomers, e.g., [vinyltrimethoxysilane, vinyltriethoxysilane, vinyltributoxysilane, vinylmethoxydimethylsilane, vinylmethoxydimethylsilane, vinylisobutoxydimethylsilane, vinylmethoxydimethylsilane, vinyltriethoxymethylsilane, vinyltris( $\beta$ -methoxyethoxy)silane, vinylbisphenylethoxysilane, vinyltriphenoxysilane,  $\gamma$ -(vinylphenylaminopropyl)trimethoxysilane,  $\gamma$ -(vinylbenzylaminopropyl)trimethoxysilane,  $\gamma$ -(vinylphenylaminopropyl)triethoxysilane,  $\gamma$ -(vinylbenzylaminopropyl)triethoxysilane, divinyltrimethoxysilane, divinyltriethoxysilane, divinylbis( $\beta$ -methoxyethoxy)silane, vinylbis(acetoxy)methylsilane, vinyltriethoxysilane, vinylbis(dimethylamino)methylsilane, vinylmethylchlorosilane, vinylmethylchlorosilane, vinyltrichlorosilane, vinylmethylphenylchlorosilane, allyltriethoxysilane, 3-allylaminopropyltrimethoxysilane, allyltriethoxymethylsilane, allyltriethoxysilane, allylbis(dimethylamino)methylsilane, allylmethylchlorosilane, allyldimethylchlorosilane, allyltrichlorosilane, methallylphenylchlorosilane,  $\beta$ -(meth)acryloxyethyltrimethoxysilane,  $\beta$ -(meth)acryloxyethyltriethoxysilane,  $\gamma$ -(meth)acryloxypropyltrimethoxysilane,  $\gamma$ -(meth)acryloxypropyltriethoxysilane,  $\gamma$ -(meth)acryloxypropylmethyltrimethoxysilane,  $\gamma$ -(meth)acryloxypropylmethyltriethoxysilane,  $\gamma$ -(meth)acryloxypropylmethylchlorosilane,  $\gamma$ -(meth)acryloxypropyltris( $\beta$ -methoxyethoxy)silane]. Those crosslinking monomers can be used independently or in a combination of two or more species.

[0027] The crosslinking monomer has as a hydrolyzable condensing group, alkoxysilyl (e.g.  $C_{1-4}$  alkoxysilyl group such as methoxysilyl and ethoxysilyl).

[0028] The hydrophilic monomer includes but is not limited to carboxyl group-containing monomers [monomers having free carboxyl groups or acid anhydride groups such as (meth)acrylic acid, itaconic acid, maleic acid, maleic anhydride, fumaric acid and crotonic acid, and the corresponding salts (alkali metal salts, alkaline earth metal salts, ammonium salts, amine salts)], half-esters of unsaturated polycarboxylic acids or acid anhydrides thereof with a straight-chain or branched alcohol containing 1 to about 20 carbon atoms [monomethyl maleate, monoethyl maleate, monobutyl maleate, monoethyl maleate, mono-2-ethylhexyl maleate], hydroxyl group-containing monomers [hydroxy- $C_{2-6}$  alkyl esters of (meth)acrylic acid including 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate and 4-hydroxybutyl (meth)acrylate], amide group-containing monomers [(meth)acrylamide,  $\alpha$ -ethyl (meth)acrylamide, N-methyl(meth)acrylamide, N-butoxymethyl(meth)acrylamide, diacetone(meth)acrylamide], sulfo-containing monomers [styrenesulfonic acid, vinylsulfonic acid], ether group-containing monomers [vinyl ethers such as vinyl methyl ether, vinyl ethyl ether and vinyl isobutyl ether], and polyoxyalkylene group-containing monomers [diethylene glycol mono(meth)acrylate, triethylene glycol mono(meth)acrylate, polyethylene glycol mono(meth)acrylate]. These hydrophilic monomers may also be used independently or in a combination of two or more species.

[0029] The preferred hydrophilic monomer includes carboxyl group-containing monomers [(meth)acrylic acid], hydroxyl group-containing monomers [2-hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate], and monomers containing a polyoxyalkylene unit [diethylene glycol mono(meth)acrylate, triethylene glycol mono(meth)acrylate, polyethylene glycol and mono(meth)acrylate].

[0030] These monomers are generally used in combination with one or more nonionic monomers for judicious control of film-forming properties and film characteristics.

**[0031]** The nonionic monomer that can be used includes, for example, alkyl esters [e.g. C<sub>1-18</sub> alkyl esters of (meth)acrylic acid such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, hexyl (meth)acrylate, octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate and stearyl (meth)acrylate], cycloalkyl esters [cyclohexyl (meth)acrylate], aryl esters [phenyl(meth)acrylate, ], aralkyl esters [benzyl (meth)acrylate], aromatic vinyl compounds [styrene, vinyltoluene,  $\alpha$ -methylstyrene], vinyl esters [vinyl acetate, vinyl propionate, vinyl versatate], allyl esters [allyl acetate], halogen-containing monomers [vinylidene chloride, vinyl chloride], vinyl cyanides [(meth)acrylonitrile] and olefins [ethylene, propylene, ].

**[0032]** These nonionic monomers can also be used independently or in a combination of two or more species.

**[0033]** As the nonionic monomer, use can be generally made of C<sub>1-18</sub> alkyl esters of (meth)acrylic acid [particularly C<sub>2-10</sub> alkyl esters of acrylic acid and C<sub>1-6</sub> alkyl esters of methacrylic acid], aromatic vinyl compounds [particularly styrene], and vinyl esters [particularly vinyl acetate].

**[0034]** The proportions of the cationic monomer, crosslinking monomer, and hydrophilic monomer can be judiciously selected from the range not detracting from water resistance and ink absorption. By way of illustration, the cationic monomer may account for 0.1 to 50 mole % (e.g. 1 to 45 mole %), preferably 0.5 to 40 mole % (e.g. 2 to 35 mole %), more preferably 1 to 30 mole % (e.g. 3 to 25 mole %), and usually about 2 to 25 mole %, of the total monomer component. The crosslinking monomer may account for 0.1 to 25 mole %, preferably 0.2 to 20 mole %, more preferably 0.5 to 15 mole %, and usually 0.3 to 10 mole %, of the total monomer component.

**[0035]** The proportion of the hydrophilic monomer may for example be 0 to 50 mole %, preferably 0 to 45 mole % (0.5 to 45 mole %), more preferably 0 to 40 mole % (1 to 35 mole %), and generally 1 to 20 mole % of the total monomer component. Usually, the nonionic monomer mentioned above accounts for the remainder of the total monomer component.

**[0036]** The glass transition temperature of the cationic monomer can be selected from the range not adversely affecting film-forming and other characteristics, and may for example be -20°C to 50°C, preferably -10°C to 40°C, and more preferably 0°C to 30°C. Polymers with such glass transition temperatures can be produced by using appropriate species of the cationic monomer and crosslinking monomer, plus, optionally, the hydrophilic monomer, in a suitable combination. Those monomers may be practically copolymerized with a hard monomer [e.g. a monomer which will give a homopolymer with a glass transition temperature of 80 to 120°C (particularly 90 to 105°C), such as methyl (meth)acrylate and styrene] and a soft monomer [e.g. a monomer which will give a homopolymer with a glass transition temperature of -85°C to -10°C (particularly -85°C to -20°C), such as C<sub>2-10</sub> alkyl ester of acrylic acid] to constitute a copolymer.

**[0037]** In using the respective monomers in combination, their proportions can be selected, for example, from within the following ranges.

(a) Cationic monomer:

1 to 40 weight % (preferably 3 to 35 weight %, particularly 5 to 30 weight %)

(b) Crosslinking monomer:

0.5 to 20 weight % (preferably 1 to 15 weight %, particularly 2 to 10 weight %)

(c) Hydrophilic monomer:

0 to 50 weight % (preferably 2 to 45 weight %, particularly 5 to 40 weight %)

(d) Hard monomer

10 to 60 weight % (preferably 20 to 55 weight %, particularly 25 to 50 weight %)

(e) Soft monomer

10 to 60 weight % (preferably 15 to 50 weight %, particularly 20 to 45 weight %)

**[0038]** The weight average molecular weight of the cationic polymer can be selected from the range of, for example,  $0.2 \times 10^4$  to  $100 \times 10^4$ , preferably  $1 \times 10^4$  to  $50 \times 10^4$ .

**[0039]** The form of the cationic polymer is a cationic emulsion (particularly an aqueous emulsion).

**[0040]** The surface potential ( $\zeta$  potential) of polymer particles in the cationic emulsion +10 to +60 mV, preferably +12

to +55 mV (e.g. +15 to +55 mV), and more preferably +20 to +55 mV. The lower the surface potential of the polymer particle is, the lower are ink fixability and water resistance, while the higher the surface potential is, the lower is ink absorption.

**[0041]** The surface potential ( $\zeta$  potential) of polymer particles can be determined, for example, under the following conditions.

Instrument: Electrophoretic light scatterin photometer, ELS-800®)

Measuring temperature: 25°C

Concentration: The emulsion is diluted with distilled water to a concentration of 0.01 to 0.05 weight % as nonvolatile matter.

Distance between electrodes: 32 mm

Electric field: 50 V/cm

**[0042]** The average diameter of polymer particles in the cationic emulsion may, for example, be about 1 to 200 nm, preferably 3 to 100 nm, and more preferably about 5 to 50 nm. The cationic emulsion containing such a cationic polymer can be prepared by the conventional technology including the method in which the above-mentioned monomers are emulsion-polymerized in an emulsion polymerization system containing a nonionic surfactant and/or a cationic surfactant and the method in which, following polymerization of the monomers, the reaction product is converted to a tertiary amine salt or a quaternary ammonium salt to provide the objective aqueous emulsion.

**[Hydrophilic polymer]**

**[0043]** When the cationic polymer emulsion and a hydrophilic polymer (a water-soluble polymer or a water-insoluble, water-absorbent polymer) are used in combination to form an ink absorbing layer, enhanced ink absorption can be insured without sacrificing water resistance in any appreciable measure.

**[0044]** The hydrophilic polymer includes but is not limited to hydrophilic naturally-occurring polymers and derivatives thereof (starch, corn starch, sodium alginate, gum arabic, gelatin, casein, dextrin), cellulose derivatives (methylcellulose, ethylcellulose, hydroxyethylcellulose, carboxymethylcellulose, cellulose sulfate, cyanoethylcellulose), vinyl alcohol-series polymers (polyvinyl alcohol, ethylene-vinyl alcohol copolymer), ethylenic polymers (ethylene-maleic anhydride copolymer), vinyl acetate-series copolymers (e.g. vinyl acetate-methyl acrylate copolymer, ), polyalkylene oxides (polyethylene oxide, ethylene oxide-propylene oxide block copolymer), carboxyl- or sulfo-containing polymers and salts thereof [acrylic polymers (poly(meth)acrylic acid or its salt (ammonium salt and alkali metal salts such as sodium salt), methyl methacrylate-(meth)acrylic acid copolymer, acrylic acid-polyvinyl alcohol copolymer), vinyl ether-series polymers (poly(vinyl alkyl ethers) such as poly(vinyl methyl ether) and poly(vinyl isobutyl ether), methyl vinyl ether-maleic anhydride copolymer), styrenic polymers (styrene-maleic anhydride copolymer, styrene-(meth)acrylic acid copolymer, poly(sodium styrenesulfonate)), poly(sodium vinylsulfonate), ], nitrogen-containing polymers (or cationic polymers) and salts thereof (quaternary ammonium salts such as polyvinylbenzyltrimethylammonium chloride, polydiallyldimethylammonium chloride, polydimethylaminoethyl (meth)acrylate hydrochloride, polyvinylpyridine, polyvinylimidazole, polyethyleneimine, polyamidepolyamine, polyacrylamide and polyvinylpyrrolidone), among others. These hydrophilic polymers can be used independently or in combination.

**[0045]** Among these hydrophilic polymers, those preferred are cellulose derivatives (particularly hydroxyethylcellulose), vinyl alcohol-series polymers (particularly polyvinyl alcohol), vinyl ester-series polymers (particularly vinyl acetate-series copolymers), polyvinylpyrrolidone.

**[0046]** Also preferred are hydrophilic polymers each having at least one functional group selected from the group consisting of the polyoxyalkylene unit, acetoacetyl group, carboxyl group, acid anhydride group, and amino group.

**[0047]** The above-mentioned vinyl ester-series polymers (e.g. vinyl acetate-series copolymers) are copolymers of vinyl esters (e.g. vinyl acetate) with another species of copolymerizable monomer and include partial hydrolyzates of such copolymers (e.g. partial hydrolyzates with degrees of saponification of about 10 to 90%). The preferred copolymerizable monomer includes hydrophilic monomers having hydrophilic groups (e.g. carboxyl and sulfo, inclusive of their salts, hydroxyl, ether). Particularly, use can be made of vinyl monomers having ether groups, particularly oxyalkylene units, in which the number of alkylene oxide units (number of moles added) is 1 to 100, preferably 2 to 80 (e.g. 5 to 80), and more preferably 5 to 70 (e.g. 10 to 50), specific examples of which are (meth)acrylic acid esters and allyl ethers.

**[0048]** The vinyl monomers having oxyalkylene units include but are not limited to diethylene glycol mono(meth)acrylate, triethylene glycol mono(meth)acrylate, polyethylene glycol mono(meth)acrylate, dipropylene glycol mono(meth)acrylate, tripropylene glycol mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, diethylene glycol mono(meth)allyl ether, triethylene glycol mono(meth)allyl ether, polyethylene glycol mono(meth)allyl ether, dipropylene glycol mono(meth)allyl ether, tripropylene glycol mono(meth)allyl ether, and polypropylene glycol mono(meth)allyl

ether. Those vinyl monomers can be used independently or in a combination of two or more species. The preferred monomers are (meth)acrylates which are vinyl monomers containing oxyethylene units as oxyalkylene unit, and particularly polyoxyalkylene (meth) allyl ethers (above all, polyoxyethylene allyl ether).

[0049] In the vinyl acetate-series copolymer, the proportion of the copolymerizable monomer can be selected from the range not adversely affecting image definition (image sharpness) and water resistance, and may for example be 0.1 to 50 mole %, preferably about 1 to 30 mole %, and more preferably 2.5 to 25 mole % (e.g. 3 to 20 mole %) of the total monomer component.

[0050] The copolymer of vinyl acetate with a vinyl monomer having a polyoxyalkylene unit (modified vinyl acetate-series resin) is commercially available under the name of OKS-7158G, ® to give an example.

[0051] The preferred hydrophilic polymer further includes hydrophilic polymers having functional groups reactive to the reactive functional groups (e.g. epoxy groups such as glycidyl group, alkoxysilyl groups) of the cationic polymer. Such hydrophilic polymers can be used, for example, in the following combinations according to the species of the reactive groups (particularly crosslinking groups) possessed by the cationic polymers.

(1) Cationic polymer: epoxy group such as glycidyl

Hydrophilic polymer: carboxyl group,  
acid anhydride, amino groups

(2) Cationic polymer: methylol group

Hydrophilic polymer: hydroxyl, carboxyl,  
acid anhydride groups

(3) Cationic polymer: hydrolyzable condensing group such as alkoxysilane

Hydrophilic polymer: hydroxyl, carboxyl groups

(4) Cationic polymer: aziridinyl group

Hydrophilic polymer: hydroxyl, carboxyl,  
amino groups

[0052] In such combinations, the cationic polymer and the hydrophilic polymer bond to or crosslink with each other to form a highly water-resistant ink absorbing layer with high ink absorption.

[0053] The preferred hydrophilic polymer reactive with the cationic polymer includes hydrophilic polymers which are self-crosslinking (cross-linkable) and contain functional groups reactive with reactive functional groups of the cationic polymer, such as the following hydrophilic polymers.

#### 1. Acetoacetyl-modified hydrophilic polymers

[0054] The acetoacetyl-modified hydrophilic polymer includes acetoacetyl-containing hydrophilic polymers obtained by a reaction of hydroxyl-containing hydrophilic polymer with an acetoacetic acid ester, such as acetoacetyl-modified vinyl acetate-series copolymers (acetoacetyl-containing polyvinyl alcohol, acetoacetyl-containing cellulose derivatives). Acetoacetyl-modified vinyl acetate-series copolymers can be purchased from commercial sources.

#### 2. Carboxyl-modified hydrophilic polymers

[0055] (2a) Carboxyl-modified polyvinyl alcohols: e.g. partial hydrolyzates of the copolymers of vinyl esters (vinyl acetate, vinyl propionate, vinyl formate) with a carboxyl-containing unsaturated monomer (a monocarboxylic acid such as (meth)acrylic acid, a dicarboxylic acid such as maleic acid, fumaric acid and itaconic acid, or an acid anhydride or alkyl monoester thereof). Such carboxyl-modified polyvinyl alcohols can be purchased from commercial sources.

[0056] The carboxyl-modified hydrophilic polymer further includes styrene-(meth)acrylic acid copolymer, (meth)acrylic acid ester-(meth)acrylic acid copolymer (e.g. methyl methacrylate-(meth)acrylic acid copolymer), vinyl acetate-(meth)acrylic acid copolymer.

[0057] (2b) Carboxyl-containing polysaccharides such as carboxy C<sub>1-4</sub> alkylcellulose, carboxymethyl dextran, and alginic acid.

#### 3. Acid anhydride group-containing hydrophilic polymer

[0058] Alkyl vinyl ether-maleic anhydride copolymers (e.g. methyl vinyl ether-maleic anhydride copolymer), ethylene-maleic anhydride copolymer, vinyl acetate-maleic anhydride copolymer, styrene-maleic anhydride copolymer, and (meth)acrylic acid ester-maleic anhydride copolymer (e.g. methyl methacrylate-maleic anhydride copolymer).

## 4. Amino-containing hydrophilic polymer

**[0059]** Polyamidopolyamines, polyvinylamines, poly(N-vinylformamide) partial hydrolyzate, amino-containing polysaccharides (aminodextran, chitosan).

**[0060]** The ratio of the cationic polymer to the hydrophilic polymer can be selected, according to the species of cationic polymer and hydrophilic polymer and the concentration of the available crosslinking groups, from the range not detracting from water resistance and ink absorption. For example, the ratio (former/latter) can be selected from the range of 5/95 to 95/5 (weight %), preferably 10/90 to 90/10 (weight %), and more preferably 20/80 to 80/20 (weight %), on a nonvolatile matter basis. The ratio is usually 10/90 to 50/50 (weight %), and particularly 20/80 to 40/60 (weight %).

**[0061]** The hydrophilic polymer may have reactive functional groups of the cationic polymer. In such cases, the cationic polymer may have functional groups corresponding to the functional groups of the hydrophilic polymer. For example, when the hydrophilic polymer is an epoxy-containing polymer, the cationic polymer may have a carboxyl or amino group. The epoxy-containing polymer includes but is not limited to hydrolyzates of the copolymers of an epoxy-containing monomer (glycidyl (meth)acrylate, allyl glycidyl ether, etc.) with vinyl esters (vinyl acetate), epoxy-containing polyvinyl alcohols in which the epoxy group is obtained by a reaction of active hydrogen (hydroxy, amino, carboxy)-containing hydrophilic polymers with epichlorohydrin, and epoxy-containing polyvinylpyrrolidones obtainable by copolymerizing the epoxy-containing monomers with vinylpyrrolidone. The epoxy content is 0.01 to 5 mole %, preferably 0.1 to 3 mole % (e.g. 0.2 to 2.5 mole %), and particularly 0.2 to 2 mole%, based on the total monomer component.

**[0062]** A curing agent (a curing catalyst or a cure accelerator) may be added to the ink absorbing layer for the promotion of the curing reaction. The curing agent that can be used includes, for example, organotin compounds (dibutyltin dilaurate, dibutyltin dimaleate, dioctyltin dilaurate, dioctyltin dimaleate, dibutyltin diacetate, dibutyltin dimethoxide, tributyltin sulfite, dibutyltin thioglycolate, stannous octanoate), organoaluminum compounds (aluminum isopropylate, aluminum tris(ethylacetoacetate), aluminum tris(acetylacetonate), ethyl acetoacetate aluminum diisopropylate), organotitanium compounds (isopropyl tris(stearyl) titanate, tetraisopropyl bis(dioctyl phosphite) titanate, bis(dioctyl pyrophosphate) oxyacetate titanate), organozirconium compounds (tetra-n-butoxyzirconium, zirconyl octanoate, reaction products of alkoxyzirconiums with acetylacetone or an acetoacetic ester), acidic compounds (organic acids such as aliphatic organic carboxylic acids, e.g. acetic acid, propionic acid, hydroxycarboxylic acids, aromatic carboxylic acids, e.g. benzoic acid, sulfonic acids, e.g. benzenesulfonic acid, p-toluenesulfonic acid, dodecylbenzenesulfonic acid, ), basic compounds (bases, for example, organic bases including triethylamine, and inorganic bases including sodium hydroxide and potassium hydroxide), acidic phosphoric acid esters (monobutyl phosphate, dibutyl phosphate, isopropyl acid phosphate, butyl acid phosphate, octyl acid phosphate, tridecyl acid phosphate), and mixtures or reaction products of the acidic phosphoric acid esters with an amine (hexylamine, triethylamine, N,N-dimethyldodecylamine, 3-propanolamine). Those curing agents can be used singly or as a mixture of two or more species.

**[0063]** The amount of the curing agent can be selected from the range conducive to acceleration of hardening, for example, from the range of 0.01 to 10 weight parts, preferably 0.1 to 5 weight parts, per 100 weight parts of the resin composition comprising the cationic polymer and the hydrophilic polymer on a nonvolatile matter basis.

**[0064]** For improved fixation of colorants (dyes), it is advantageous to use a dye fixing agent (dye fixative), particularly a macromolecular dye fixing agent or high molecular weight dye fixative. Dye fixatives (high molecular weight dye fixatives) usually contain cationic groups (particularly strongly cationic groups such as guanidyl or quaternary ammonium salt groups) in the molecule. The dye fixative may be soluble in water.

**[0065]** The dye fixative thus includes but is not limited to dicyan-series fixatives (dicyandiamide-formaldehyde polycondensate), polyamine-series fixatives [aliphatic polyamines such as diethylenetriamine, triethylenetetramine, dipropylenetriamine and polyallylamine, aromatic polyamines such as phenylenediamine, dicyandiamide-(poly) $C_{2-4}$  alkylenepolyamine condensates (dicyandiamide-diethylenetriamine polycondensate)], and polycation-series fixatives. The polycation-series fixative includes but is not limited to epichlorohydrin-di- $C_{1-4}$  alkylamine addition polymers (epichlorohydrin-dimethylamine addition polymer), polymers of allylamine or its salt (a polymer of polyallylamine or its hydrochloride such as PAA-10C®, PAA-HCl-3L®, PAA-HCl-10L®), polymers of diallyl- $C_{1-4}$  alkylamine or its salt (e.g. a polymer of diallylmethylamine or its hydrochloride, such as PAS-M-1®), polymers of diallyl-di- $C_{1-4}$  alkylammonium salts (diallyldimethylammonium chloride polymer, e.g. PAS-H-5L®, PAS-H-10L®, ), copolymers of diallylamine or its salt with sulfur dioxide (diallylamine hydrochloride-sulfur dioxide copolymer, e.g. PAS-92®), diallyl  $C_{1-4}$  alkylammonium salt-sulfur dioxide copolymers (e.g. diallyldimethylammonium chloride-sulfur dioxide copolymer such as PAS-A-1®, PAS-A-5®, PAS-A-120L®, PAS-A-120A®, ), copolymers of diallyl-di- $C_{1-4}$  alkylammonium salts with diallylamine or a salt or derivative thereof (e.g. a copolymer of diallyldimethylammonium chloride-diallylamine hydrochloride derivative such as PAS-880®), polymers of diallyl-di- $C_{1-4}$  alkylammonium salts, polymers of di- $C_{1-4}$  alkylaminoethyl(meth)acrylate quaternary salts, diallyl-di- $C_{1-4}$  alkylammonium salt-acrylamide copolymers (diallyldimethylammonium chloride-acrylamide copolymer, such as PAS-J-81®), and amine-carboxylic acid copolymers (e.g. PAS-410®). Those dye fixatives can also be used independently or in a combination of two or more species.



[0066] The amount of the dye fixative can be selected from the range conducive to improved fixation, for example the range of 0.1 to 40 weight parts, preferably 1 to 30 weight parts, and more preferably about 20 weight parts, on a nonvolatile matter basis, per 100 weight parts of the resin composition comprising the cationic polymer and the hydrophilic polymer.

[0067] Where necessary, the ink absorbing layer may be supplemented with other ingredients, such as a polymer having no crosslinking group or an aqueous emulsion containing polymer particles (e.g. acrylic resin emulsion, ethylene-vinyl acetate copolymer emulsion, vinyl acetate-series emulsion).

[0068] A particulate substance (e.g. a pigment) may be incorporated in the ink absorbing layer. The particulate substance includes, for example, inorganic powders (particulate minerals such as white carbon, finely divided calcium silicate, zeolite, magnesium aluminosilicate, calcined diatomite, finely divided magnesium carbonate, finely divided alumina, silica, talc, kaolin, delaminated kaolin, clay, heavy calcium carbonate, light calcium carbonate, magnesium carbonate, titanium dioxide, aluminum hydroxide, calcium hydroxide, magnesium hydroxide, magnesium silicate, calcium sulfate, sericite, bentonite, smectite), and organic powders (organic particles such as finely divided organic powders of crosslinked or non-crosslinked polystyrene, acrylic, urea, melamine, benzoguanamine, and other resins and microfine hollow powders). Those particulate substances can be selectively used independently or in a suitable combination of two or more species. When a particulate substance is used, the hydrophilic polymer mentioned hereinbefore can be used as a binder resin.

[0069] The ratio of the particulate substance to the binder resin may, for example, be 0.1 to 80 weight parts, preferably 0.2 to 50 parts of the particulate substance relative to 100 weight parts of the binder resin.

[0070] The ink absorbing layer may further contain the conventional additives, such as an antifoam, a coatability improving agent, a thickener, a lubricant, a stabilizer (antioxidant, ultraviolet absorber, heat stabilizer), an antistatic, and an antiblocking agent each in a proportion not adversely affecting the characteristics of the ink absorbing layer.

[0071] The thickness of the ink absorbing layer can be selected according to the intended application and may for example be 5 to 50  $\mu\text{m}$ , preferably 10 to 30  $\mu\text{m}$ , and usually 5 to 30  $\mu\text{m}$ .

[0072] Being equipped with the above ink absorbing layer, the recording sheet of the present invention features high ink absorption and high ink fixation properties and, at the same time, has been remarkably improved in water resistance. Thus, when a printing or image, formed with a water-based ink by an ink jet recording system and dried, is immersed in water at a temperature of 30°C for 1 minute, the recording sheet shows a color density retention rate of not less than 80% (e.g. 85 to 100%), preferably not less than 85% (e.g. 90 to 99%).

#### [Production Technology]

[0073] The recording sheet of the present invention can be manufactured by constructing, on at least one side of the substrate, (1) an ink absorbing layer comprising the crosslinking group-containing cationic polymer and the hydrophilic polymer, (2) an ink absorbing layer comprising the crosslinking group- and hydrophilic group-containing cationic polymer and the hydrophilic polymer,

[0074] Any of the above ink absorbing layers can be formed by coating the substrate or support with a coating composition prepared with the use of a suitable solvent i.e., a water-based or aqueous coating composition is employed. The coating composition is cast or coated on at least one side of the substrate by roll coating, air knife coating, blade coating, rod coating, bar coating, comma coating, gravure coating, silk screen coating, or other conventional casting or coating techniques.

[0075] The ink absorbing layer can be provided by applying a coating composition containing the ingredients to at least one side of the substrate and drying the coating. Where necessary, a crosslinked ink absorbing layer may be provided by heating the coated substrate at a suitable temperature selected from the range of 50 to 150°C.

[0076] Where necessary, a porous layer, an antiblocking layer, a lubrication or slipping layer, or an antistatic layer may be superimposed on the ink absorbing layer.

[0077] In accordance with the present invention, the ink absorbing layer is constructed from a cationic polymer containing crosslinking groups, whereby water resistance and ink absorption show marked improvements. Moreover, the conflicting parameters of water resistance and ink absorbability are reconciled, while improved print quality are ensured. Therefore, the recording sheet of the present invention is not only valuable as a recording sheet for the ink jet recording system in which flying droplets of ink are used to make a record, but also useful as printing sheets (particularly sheets for water-based inks) for offset printing, flexography or other printing methods.

#### EXAMPLES

[0078] The following examples are intended to illustrate the present invention in further detail and should by no means be construed as defining the scope of the invention.

[0079] In the examples, the term "part(s)" indicates part(s) by weight. The various quality parameters of the recording

sheets prepared in the examples and comparative examples were determined and evaluated by the following methods.  
**[0080]** Using an ink jet printer (BJC-420J, ®), a solid record image in each color of cyan, yellow, magenta and black was printed on the recording sheet obtained in the examples and comparative examples.

5 (Ink absorption)

**[0081]** At every predetermined period of time after printing, PPC copying paper was set on the printed portion and a load (250 g/cm<sup>2</sup>) was imposed on the copying paper for 10 seconds. The copying paper was then removed and visually inspected for offset. The ink absorption was evaluated in terms of the time when offset was no longer observed.

10

(Water resistance)

**[0082]** After printing, the print was wiped with a water-soaked cotton swab in 10 reciprocations and the degree of deinking (ink removal) was visually evaluated.

15

- O: Unchanged
- Δ: Some deinking has made the print pale
- X: The print has been wiped out

20 (Print quality)

**[0083]** The quality of the print was visually evaluated according to the following criteria.

- O: Uniform print
- Δ: Somewhat uneven print
- X: Considerably uneven print

25

(Water immersion test)

30 **[0084]** The printed portion was immersed in water at 30°C for 1 minute, then raised vertically out of the water, drained well, and dried. After being dried, the print was visually evaluated according to the following criteria.

- O: The print remains intact
- Δ: The print is blurred
- X: No print remained

35

(Color density retention)

40 **[0085]** The color density of the print was measured with the reflectance type Macbeth densitometer RD-1255 (®). The color density was expressed in the sum of the maximum reflected densities of cyan, yellow, magenta, and black. The printed part was immersed in water at 30°C for 1 minute, raised vertically from the water, drained well, and dried. After being dried, the color density was similarly determined and the color density retention rate was calculated by means of the following equation.

45

Color density retention (%) =

(color density after immersion /

50

color density before immersion) x 100

#### Example 1

(1) Cationic acrylic copolymer emulsion 1

55

**[0086]** A 2,000 ml reactor equipped with a stirrer, a reflux condenser, a drip funnel, a nitrogen gas inlet pipe, and a thermometer was charged with 219 parts of isopropyl alcohol (IPA) and 1.23 parts of azoisobutyronitrile (AIBN). The charge was dissolved by stirring and heated to 80°C. As a copolymerization component, a mixture of 93.7 parts of

5 methyl methacrylate (MMA), 98.7 parts of n-butyl acrylate (BA), 49.3 parts of diethylaminoethyl methacrylate (DEAE-MA), and 4.93 parts of trimethoxysilanepropyl methacrylate (A-174®; hereinafter sometimes referred to briefly as A-174) was fed dropwise into the reactor over about 4 hours. After completion of the dropwise addition, a solution mixture of 0.25 part of AIBN and 25 parts of IPA was further added dropwise as an additional catalyst, and the reaction was continued for another 2 hours to complete the polymerization reaction.

10 [0087] After completion of the polymerization, 16 parts of acetic acid was fed into the flask with constant stirring and, thereafter, 705 parts of water was introduced dropwise over about 2 hours for emulsification. From the resulting emulsion, IPA was evaporated off on a rotary evaporator to provide a cationic acrylic copolymer emulsion 1 (nonvolatile matter 34.7%). The surface potential ( $\zeta$  potential) of the polymer particles of this emulsion was +23 mV, as determined under the above-described conditions.

#### (2) Recording sheet 1A

15 [0088] A water-based coating composition was prepared by mixing 86.5 parts (nonvolatile matter 30 parts) of the cationic acrylic copolymer emulsion 1 obtained in the above step (1) with 700 parts (nonvolatile matter 70 parts) of a 10 weight % aqueous solution of acetoacetyl-modified vinyl acetate-series copolymer (Z-320®).

[0089] The above water-based coating composition was coated on a 100  $\mu\text{m}$ -thick polyethylene terephthalate film pretreated for increased bonding affinity (Mellinex 705®; hereinafter sometimes referred to briefly as PET film) and dried at 100°C for 3 minutes to provide a recording sheet 1A having a 15  $\mu\text{m}$ -thick ink absorbing layer.

#### (3) Recording sheet 1B

20 [0090] A water-based coating composition was prepared by mixing 72.0 parts (nonvolatile matter 25 parts) of the cationic acrylic copolymer emulsion 1 obtained in the above step (1) with 500 parts (nonvolatile matter 75 parts) of a 15 weight % aqueous solution of a modified vinyl acetate-series copolymer (OKS-7158G®). This water-based coating composition was coated on a PET film and dried at 100°C for 3 minutes to provide a recording sheet 1B having a 15  $\mu\text{m}$ -thick ink absorbing layer.

#### (4) Recording sheet 1C

30 [0091] A water-based coating composition was prepared by mixing 72.0 parts (nonvolatile matter 25 parts) of the cationic acrylic copolymer emulsion 1 obtained in the above step (1) with 750 parts (nonvolatile matter 75 parts) of a 10 weight % aqueous solution of polyvinylpyrrolidone (weight average molecular weight  $36 \times 10^4$ ). This water-based coating composition was coated on a PET film and dried at 100°C for 3 minutes to provide a recording sheet 1C having a 15  $\mu\text{m}$ -thick ink absorbing layer.

#### (5) Recording sheet 1D

40 [0092] A water-based coating composition was prepared by mixing 115.3 parts (nonvolatile matter 40 parts) of the cationic acrylic copolymer emulsion 1 obtained in the above step (1), 400 parts (nonvolatile matter 60 parts) of a 15 weight % aqueous solution of a modified vinyl acetate-series copolymer (OKS-7158G®), 4 parts of a curing- or crosslinking-accelerator (paratoluenesulfonic acid), and 0.4 part of a particulate substance (crosslinked poly(methyl methacrylate) MBX-20®). This water-based coating composition was coated on a PET film and dried at 100°C for 3 minutes to provide a recording sheet 1D having a 15  $\mu\text{m}$ -thick ink absorbing layer.

#### (6) Recording sheet 1E

50 [0093] A water-based coating composition was prepared by mixing 115.3 parts (nonvolatile matter 40 parts) of the cationic acrylic copolymer emulsion 1 obtained in the above step (1), 600 parts (nonvolatile matter 60 parts) of a 10 weight % aqueous solution of an acetoacetyl-modified vinyl acetate-series copolymer (Z-320®), and 35.7 parts (nonvolatile matter 10 parts) of a 28 weight % aqueous solution of a dye fixative (PAS-H-5L®). This water-based coating composition was coated on a PET film and dried at 100°C for 3 minutes to provide a recording sheet 1E having a 15  $\mu\text{m}$ -thick ink absorbing layer.

## Example 2

## (1) Cationic acrylic copolymer emulsion 2

[0094] Except for using, as copolymerization components, 71.6 parts of MMA, 71.6 parts of BA, 49.3 parts of DE-AEMA, 49.3 parts of polyethylene glycol methacrylate (Blemmer PEG-200®; hereinafter sometimes referred to briefly as PEG-200), and 4.9 parts of "A-174," the procedure of Example 1 was repeated to provide a cationic acrylic copolymer emulsion 2 (nonvolatile matter 31.9%). The surface potential ( $\zeta$  potential) of the polymer particles of the emulsion was +32 mV, as determined under the conditions mentioned hereinbefore.

## (2) Recording sheet 2A

[0095] The cationic acrylic copolymer emulsion 2 obtained in the above step (1) was coated on a PET film and dried at 100°C for 3 minutes to provide a recording sheet 2A having a 15  $\mu$ m-thick ink absorbing layer.

## (3) Recording sheet 2B

[0096] A water-based coating composition was prepared by mixing 125.4 parts (nonvolatile matter 40 parts) of the cationic acrylic copolymer emulsion 2 obtained in the above step (1) with 600 parts (nonvolatile matter 60 parts) of a 10 weight % aqueous solution of an acetoacetyl-modified vinyl acetate-series copolymer (Z-320®). This water-based coating composition was coated on a PET film and dried at 100°C for 3 minutes to provide a recording sheet 2B having a 15  $\mu$ m-thick ink absorbing layer.

## (4) Recording sheet 2C

[0097] A water-based coating composition was prepared by mixing 78.4 parts (nonvolatile matter 25 parts) of the cationic acrylic copolymer emulsion 2 obtained in the above step (1) with 500 parts (nonvolatile matter 75 parts) of a 15 weight % aqueous solution of a modified vinyl acetate-series copolymer (OKS-7158G®). This water-based coating composition was coated on a PET film and dried at 100°C for 3 minutes to provide a recording sheet 2C having a 15  $\mu$ m-thick ink absorbing layer.

## (5) Recording sheet 2D

[0098] A water-based coating composition was prepared by mixing 156.7 parts (nonvolatile matter 50 parts) of the cationic acrylic copolymer emulsion 2 obtained in the above step (1) with 500 parts (nonvolatile matter 50 parts) of a 10 weight % aqueous solution of polyvinylpyrrolidone (weight average molecular weight  $36 \times 10^4$ ). This water-based coating composition was coated on a PET film and dried at 100°C for 3 minutes to provide a recording sheet 2D having a 15  $\mu$ m-thick ink absorbing layer.

## (6) Recording sheet 2E

[0099] A water-based coating composition was prepared by mixing 125.4 parts (nonvolatile matter 40 parts) of the cationic acrylic copolymer emulsion 2 obtained in the above step (1), 600 parts (nonvolatile matter 60 parts) of a 10 weight % aqueous solution of an acetoacetyl-modified vinyl acetate-series copolymer (Z-320®), and 0.5 part of a curing catalyst (dioctyltin dilaurate). This water-based coating composition was coated on a PET film and dried at 100°C for 3 minutes to provide a recording sheet 2E having a 15  $\mu$ m-thick ink absorbing layer.

## Example 3

## (1) Cationic acrylic copolymer emulsion 3

[0100] Except for using, as copolymerization components, 71.6 parts of MMA, 71.6 parts of BA, 49.3 parts of DE-AEMA, 49.3 parts of 2-hydroxyethyl methacrylate, and 2.5 parts of "A-174," the procedure of Example 1 was repeated to provide a cationic acrylic copolymer emulsion 3 (nonvolatile matter 26.9%). The surface potential ( $\zeta$  potential) of the polymer particles of the emulsion was +35 mV, as determined under the conditions mentioned hereinbefore.

## (2) Recording sheet 3A

[0101] The cationic acrylic copolymer emulsion 3 obtained in the above step (1) was coated on a PET film and dried at 100°C for 3 minutes to provide a recording sheet 3A having a 15 µm-thick ink absorbing layer.

## (3) Recording sheet 3B

[0102] A water-based coating composition was prepared by mixing 148.7 parts (nonvolatile matter 40 parts) of the cationic acrylic copolymer emulsion 3 obtained in the above step (1) with 600 parts (nonvolatile matter 60 parts) of a 10 weight % aqueous solution of an acetoacetyl-modified vinyl acetate-series copolymer (Z-320®). This water-based coating composition was coated on a PET film and dried at 100°C for 3 minutes to provide a recording sheet 3B having a 15 µm-thick ink absorbing layer.

## (4) Recording sheet 3C

[0103] A water-based coating composition was prepared by mixing 92.9 parts (nonvolatile matter 25 parts) of the cationic acrylic copolymer emulsion 3 obtained in the above step (1) with 500 parts (nonvolatile matter 75 parts) of a 15 weight % aqueous solution of a modified vinyl acetate-series copolymer (OKS-7158G®). This water-based coating composition was coated on a PET film and dried at 100°C for 3 minutes to provide a recording sheet 3C having a 15 µm-thick ink absorbing layer.

## (5) Recording sheet 3D

[0104] A water-based coating composition was prepared by mixing 92.9 parts (nonvolatile matter 25 parts) of the cationic acrylic copolymer emulsion 3 obtained in the above step (1) with 750 parts (nonvolatile matter 75 parts) of a 10 weight % aqueous solution of polyvinylpyrrolidone (weight average molecular weight  $36 \times 10^4$ ). This water-based coating composition was coated on a PET film and dried at 100°C for 3 minutes to provide a recording sheet 3D having a 15 µm-thick ink absorbing layer.

## Example 4

## (1) Cationic acrylic copolymer emulsion 4

[0105] Using 59.1 parts of MMA, 59.1 parts of BA, 49.3 parts of DEAEMA, 49.3 parts of PEG-200, 24.7 parts of acrylic acid, and 4.9 parts of "A-174", polymerization was carried out in the same manner as in Example 1.

[0106] After completion of the polymerization, the flask was charged with 5.8 parts of 25% aqueous ammonia with stirring, and 705 parts of water was added dropwise over about 2 hours for emulsification. The resulting emulsion was concentrated in the same manner as in Example 1 to provide a cationic acrylic copolymer emulsion 4 (nonvolatile matter 34.0%). The surface potential ( $\zeta$  potential) of polymer particles of this emulsion was +15 mV, as determined under the conditions mentioned hereinbefore.

## (2) Recording sheet 4A

[0107] The cationic acrylic copolymer emulsion 4 obtained in the above step (1) was coated on a PET film and dried at 100°C for 3 minutes to provide a recording sheet 4A having a 15 µm-thick ink absorbing layer.

## (3) Recording sheet 4B

[0108] A water-based coating composition was prepared by mixing 88.2 parts (nonvolatile matter 30 parts) of the cationic acrylic copolymer emulsion 4 obtained in the above step (1) with 700 parts (nonvolatile matter 70 parts) of a 10 weight % aqueous solution of acetoacetyl-modified vinyl acetate-series copolymer (Z-320®). This water-based coating composition was coated on a PET film and dried at 100°C for 3 minutes to provide a recording sheet 4B having a 15 µm-thick ink absorbing layer.

## (4) Recording sheet 4C

[0109] A water-based coating composition was prepared by mixing 88.2 parts (nonvolatile matter 30 parts) of the cationic acrylic copolymer emulsion 4 obtained in the above step (1) with 466.7 parts (nonvolatile matter 70 parts) of

a 15 weight % aqueous solution of modified vinyl acetate-series copolymer (OKS-7158G®). This water-based coating composition was coated on a PET film and dried at 100°C for 3 minutes to provide a recording sheet 4C having a 15 µm-thick ink absorbing layer.

#### (5) Recording sheet 4D

[0110] A water-based coating composition was prepared by mixing 73.5 parts (nonvolatile matter 25 parts) of the cationic acrylic copolymer emulsion 4 obtained in the above step (1) with 750 parts (nonvolatile matter 75 parts) of a 10 weight % aqueous solution of polyvinylpyrrolidone (weight average molecular weight  $36 \times 10^4$ ). This water-based coating composition was coated on a PET film and dried at 100°C for 3 minutes to provide a recording sheet 4D having a 15 µm-thick ink absorbing layer.

#### Comparative Example 1

#### (1) Acrylic copolymer emulsion 5

[0111] A 2,000 ml reactor equipped with a stirrer, a reflux condenser, a drip funnel, a nitrogen gas inlet pipe, and a thermometer was charged with 679 parts of water, followed by addition of 0.75 part of polyoxyethylene nonylphenyl ether and 2.8 parts of alkyl diphenyl ether sulfonate sodium, and the charge was thoroughly dissolved by stirring. Then, 60 parts of MMA and 60 parts of BA were added and the mixture was heated to 50°C. To this mixture was added 0.3 g of potassium persulfate to start polymerization. After 2 hours of reaction, 0.3 g of potassium persulfate was further added and the mixture was reacted for 3 hours to complete the polymerisation, whereby an acrylic copolymer emulsion 5 (nonvolatile matter 16.8%) was obtained. The surface potential ( $\zeta$  potential) of polymer particles of the emulsion was -18 mV, as determined under the same conditions as above.

#### (2) Recording sheet 5A

[0112] The acrylic copolymer emulsion 5 obtained in the above step (1) was coated on a PET film and dried at 100°C for 3 minutes to provide a recording sheet 5A having a 15 µm-thick ink absorbing layer.

#### (3) Recording sheet 5B

[0113] A water-based coating composition was prepared by mixing 148.8 parts (nonvolatile matter 25 parts) of the acrylic copolymer emulsion 5 obtained in the above step (1) with 750 parts (nonvolatile matter 75 parts) of a 10 weight % aqueous solution of acetoacetyl-modified vinyl acetate-series copolymer (Z-320®). This water-based coating composition was coated on a PET film and dried at 100°C for 3 minutes to provide a recording sheet 5B having a 15 µm-thick ink absorbing layer.

#### (4) Recording sheet 5C

[0114] A water-based coating composition was prepared by mixing 148.8 parts (nonvolatile matter 25 parts) of the acrylic copolymer emulsion 5 obtained in the above step (1) with 500 parts (nonvolatile matter 75 parts) of a 15 weight % aqueous solution of modified vinyl acetate-series copolymer (OKS-7158G®). This water-based coating composition was coated on a PET film and dried at 100°C for 3 minutes to provide a recording sheet 5C having a 15 µm-thick ink absorbing layer.

#### (5) Recording sheet 5D

[0115] A water-based coating composition was prepared by mixing 148.8 parts (nonvolatile matter 25 parts) of the acrylic copolymer emulsion 5 obtained in the above step (1) with 750 parts (nonvolatile matter 75 parts) of a 10 weight % aqueous solution of polyvinylpyrrolidone (weight average molecular weight  $36 \times 10^4$ ). This water-based coating composition was coated on a PET film and dried at 100°C for 3 minutes to provide a recording sheet 5D having a 15 µm-thick ink absorbing layer.

#### Comparative Example 2

[0116] A 15 weight % aqueous solution of modified vinyl acetate-series copolymer (OKS-7158G®) was coated on a PET film and dried at 100°C for 3 minutes to provide a recording sheet 6 having a 15 µm-thick ink absorbing layer.

Comparative Example 3

[0117] A 10 weight % aqueous solution of acetoacetyl-modified vinyl acetate-series copolymer (Z-320®) was coated on a PET film and dried at 100°C for 3 minutes to provide a recording sheet 7 having a 15 µm-thick ink absorbing layer.

Comparative Example 4

[0118] A 10 weight % aqueous solution of polyvinylpyrrolidone (weight average molecular weight  $36 \times 10^4$ ) was coated on a PET film and dried at 100°C for 3 minutes to provide a recording sheet 8 having a 15 µm-thick ink absorbing layer.

[0119] The results of evaluation of the recording sheets obtained in the above examples and comparative examples are presented in Table 1.

Table 1

Recording sheet	Ink absorption	Water resistance	Print quality	Water immersion test	Color density retention
Example 1					
1A	3 mins.	○	○	○	97%
1B	3 mins.	△	○	△	93%
1C	4 mins.	△	△	△	92%
1D	3 mins.	○	○	○	95%
1E	4 mins.	○	○	○	100%
Example 2					
2A	5 mins.	○	△	○	95%
2B	2 mins.	○	○	○	90%
2C	2 mins.	△	○	△	92%
2D	3 mins.	△	△	△	88%
2E	3 mins.	○	○	○	94%
Example 3					
3A	5 mins.	○	△	○	95%
3B	2 mins.	○	○	○	92%
3C	2 mins.	△	○	△	87%
3D	3 mins.	△	△	△	85%
Example 4					
4A	5 mins.	○	△	○	92%
4B	2 mins.	○	○	○	88%
4C	2 mins.	△	○	△	85%
4D	3 mins.	△	△	△	85%
Comp.Ex. 1					
5A	≥7 mins.	X	X	X	30%
5B	5 mins.	X	△	X	23%
5C	5 mins.	X	△	X	25%
5D	6 mins.	X	X	X	18%
Comp.Ex. 2					
6	2 mins.	X	○	X	25%
Comp.Ex. 3					
7	2 mins.	X	○	X	28%
Comp.Ex. 4					
8	3 mins.	X	△	X	20%

[0120] It is apparent from this table that the recording sheets obtained in the examples are invariably superior to the sheets obtained in the comparative examples in water resistance and ink absorption.



## Claims

1. A recording sheet comprising a substrate and an ink absorbing layer formed on at least one side of the substrate, wherein said ink absorbing layer is obtainable from a coating composition comprising:
  - an aqueous cationic polymer emulsion having a surface potential ( $\zeta$  potential) of 10 to 60 mV, wherein the cationic polymer is a copolymer of monomers comprising either:
    - (1) a cationic monomer having tertiary amine salt groups or quaternary ammonium salt groups and a crosslinking monomer having an alkoxysilyl group, or
    - (2) a cationic monomer having tertiary amine salt groups or quaternary ammonium salt groups, a crosslinking monomer having an alkoxysilyl group, and a hydrophilic monomer; and
  - a hydrophilic polymer.
2. The recording sheet of claim 1, wherein the cationic polymer comprises an acrylic polymer emulsion.
3. The recording sheet of claim 1 or 2, wherein the hydrophilic monomer is a (meth)acrylic acid ester having a polyoxyalkylene unit.
4. The recording sheet of any of claims 1 to 3, wherein the cationic polymer is bonded to or crosslinked with the hydrophilic polymer.
5. The recording sheet of any of claims 1 to 4, wherein the cationic polymer and the hydrophilic polymer have mutually reactive functional groups.
6. The recording sheet of any of claims 1 to 5, wherein the cationic polymer is a copolymer comprising 0.1 to 50 mole % of a monomer containing a tertiary amino group or quaternary ammonium salt group and 0.1 to 25 mole % of a crosslinking monomer containing an alkoxysilyl group, wherein the tertiary amino group is convertible to a tertiary amine salt group or a quaternary ammonium salt group in the copolymer.
7. The recording sheet of any of claims 1 to 6, wherein the weight average molecular weight of the cationic polymer is  $0.2 \times 10^4$  to  $100 \times 10^4$ .
8. The recording sheet of any of claims 1 to 7, wherein the glass transition temperature of the cationic polymer is  $-20^\circ\text{C}$  to  $50^\circ\text{C}$ .
9. The recording sheet of any of claims 1 to 8, wherein the hydrophilic polymer is at least one member selected from the group consisting of cellulose derivatives, vinyl alcohol-series polymers, vinyl ester-series polymers, and polyvinylpyrrolidone.
10. The recording sheet of any of claims 1 to 9, wherein the hydrophilic polymer is a polymer having at least one functional group selected from the group consisting of a polyoxyalkylene unit, an acetoacetyl group, a carboxyl group, an acid anhydride group, and an amino group.
11. The recording sheet of any of claims 1 to 10, wherein the ratio of the cationic polymer to the hydrophilic polymer is 5/95 to 95/5 (former/latter, weight %) on a nonvolatile matter basis.
12. The recording sheet of any of claims 1 to 11, wherein the ink absorbing layer further contains a curing agent.
13. The recording sheet of any of claims 1 to 12, wherein the ink absorbing layer further contains a dye fixative.
14. A method of manufacturing the recording sheet of any of claims 1 to 13 which comprises forming an ink absorbing layer on at least one side of a substrate, wherein the ink absorbing layer has the composition of said ink absorbing layer in any of claims 1-13.
15. A composition for forming an ink absorbing layer of a recording sheet, which comprises:

- an aqueous cationic polymer emulsion having a surface potential ( $\zeta$  potential) of 10 to 60 mV, wherein the cationic polymer is a copolymer of monomers comprising either:

(1) a cationic monomer having tertiary amine salt groups or quaternary ammonium salt groups and a crosslinking monomer having an alkoxysilyl group, or

(2) a cationic monomer having tertiary amine salt groups or quaternary ammonium salt groups, a crosslinking monomer having an alkoxysilyl group, and a hydrophilic monomer; and

- a hydrophilic polymer.

#### Patentansprüche

1. Aufzeichnungsschicht, umfassend ein Substrat und eine Tinte/Farbe absorbierende Schicht, die auf wenigstens einer Seite des Substrats gebildet wird, worin die Tinte/Farbe absorbierende Schicht erhältlich ist aus einer Überzugszusammensetzung, die umfaßt:

- eine wäßrige kationische Polymer-Emulsion mit einem Oberflächenpotential ( $\zeta$ -Potential) von 10 bis 60 mV, worin das kationische Polymer ein Copolymer aus Monomeren ist, die umfassen entweder:

(1) ein kationisches Monomer, das tertiäre Amin-Salz-Gruppen oder quaternäre Ammonium-Salz-Gruppen aufweist, und ein vernetzendes Monomer, das eine Alkoxysilyl-Gruppe aufweist, oder

(2) ein kationisches Monomer, das tertiäre Amin-Salz-Gruppen oder quaternäre Ammonium-Salz-Gruppen aufweist, ein vernetzendes Monomer mit einer Alkoxysilyl-Gruppe und ein hydrophiles Monomer; und

- ein hydrophiles Polymer.

2. Aufzeichnungsschicht nach Anspruch 1, worin das kationische Polymer eine Acryl-Polymer-Emulsion umfaßt.

3. Aufzeichnungsschicht nach Anspruch 1 oder 2, worin das hydrophile Monomer ein (Meth-) Acrylsäureester mit einer Polyoxyalkylen-Einheit ist.

4. Aufzeichnungsschicht nach einem der Ansprüche 1 bis 3, worin das kationische Polymer gebunden ist an oder vernetzt ist mit dem hydrophilen Polymer.

5. Aufzeichnungsschicht nach einem der Ansprüche 1 bis 4, worin das kationische Polymer und das hydrophile Polymer wechselseitig reaktive funktionelle Gruppen aufweisen.

6. Aufzeichnungsschicht nach einem der Ansprüche 1 bis 5, worin das kationische Polymer ein Copolymer ist, das 0,1 bis 50 Mol-% eines Monomers umfaßt, das eine tertiäre Amino-Gruppe oder quaternäre Ammoniumsalz-Gruppe enthält, und 0,1 bis 25 Mol-% eines vernetzenden Monomers umfaßt, das eine Alkoxysilyl-Gruppe enthält, worin die tertiäre Amino-Gruppe in eine tertiäre Amin-Salz-Gruppe oder eine quaternäre Ammonium-Salz-Gruppe umwandelbar ist.

7. Aufzeichnungsschicht nach einem der Ansprüche 1 bis 6, worin das Gewichtsmittel des Molekulargewichts des kationischen Polymers  $0,2 \times 10^4$  bis  $100 \times 10^4$  beträgt.

8. Aufzeichnungsschicht nach einem der Ansprüche 1 bis 7, worin die Glasübergangstemperatur des kationischen Polymers  $-20^\circ\text{C}$  bis  $50^\circ\text{C}$  ist.

9. Aufzeichnungsschicht nach einem der Ansprüche 1 bis 8, worin das hydrophile Polymer wenigstens eine Verbindung ist, die gewählt ist aus der Gruppe, die besteht aus Cellulose-Derivaten, Polymeren der Vinylalkohol-Reihe, Polymeren der Vinylester-Reihe und Polyvinylpyrrolidon.

10. Aufzeichnungsschicht nach einem der Ansprüche 1 bis 9, worin das hydrophile Polymer ein Polymer ist, das wenigstens eine funktionelle Gruppe aufweist, die gewählt ist aus der Gruppe, die besteht aus einer Polyoxyalkylen-Einheit, einer Acetoacetyl-Gruppe, einer Carboxyl-Gruppe, einer Säureanhydrid-Gruppe und einer Amino-Gruppe.

11. Aufzeichnungsschicht nach einem der Ansprüche 1 bis 10, worin das Verhältnis des kationischen Polymers zu dem hydrophilen Polymer 5/95 bis 95/5 (das erstgenannte/das letztgenannte; Gew.-%) auf Basis nicht-flüchtigen Materials beträgt.

12. Aufzeichnungsschicht nach einem der Ansprüche 1 bis 11, worin die Tinte/Farbe absorbierende Schicht weiter ein Härtungsmittel umfaßt.

13. Aufzeichnungsschicht nach einem der Ansprüche 1 bis 12, worin die Tinte/Farbe absorbierende Schicht weiter ein Farbstoff-Fixativ umfaßt.

14. Verfahren zum Herstellen der Aufzeichnungsschicht nach einem der Ansprüche 1 bis 13, welches das Bilden einer Tinte/Farbe absorbierenden Schicht auf wenigstens einer Seite eines Substrats umfaßt, worin die Tinte/Farbe absorbierende Schicht die Zusammensetzung der Tinte/Farbe absorbierenden Schicht in einem der Ansprüche 1 bis 13 aufweist.

15. Zusammensetzung zum Bilden einer Tinte/Farbe absorbierenden Schicht von einer Aufzeichnungsschicht, welche umfaßt:

- eine wäßrige kationische Polymer-Emulsion mit einem Oberflächenpotential ( $\zeta$ -Potential) von 10 bis 60 mV, worin das kationische Polymer ein Copolymer aus Monomeren ist, die umfassen entweder:

(1) ein kationisches Monomer, das tertiäre Amin-Salz-Gruppen oder quaternäre Ammonium-Salz-Gruppen aufweist, und ein vernetzendes Monomer, das eine Alkoxysilyl-Gruppe aufweist, oder

(2) ein kationisches Monomer, das tertiäre Amin-Salz-Gruppen oder quaternäre Ammonium-Salz-Gruppen aufweist, ein vernetzendes Monomer mit einer Alkoxysilyl-Gruppe und ein hydrophiles Monomer; und

- ein hydrophiles Polymer.

## Revendications

1. Feuille d'enregistrement comprenant un substrat et une couche absorbant l'encre formée sur au moins une face du substrat, dans laquelle ladite couche absorbant l'encre est susceptible d'être obtenue à partir d'une composition de revêtement comprenant:

- une émulsion aqueuse de polymère cationique ayant un potentiel de surface (potentiel  $\zeta$ ) de 10 à 60 mV, dans laquelle le polymère cationique est un copolymère de monomères comprenant, soit

(1) un monomère cationique comportant des groupes sel d'amine tertiaire ou des groupes sel d'ammonium quaternaire et un monomère de réticulation comportant un groupe alcoxysilyle, soit

(2) un monomère cationique comportant des groupes sel amine tertiaire ou des groupes sel d'ammonium quaternaire, un monomère de réticulation comportant un groupe alcoxysilyle et un monomère hydrophile; et

- un polymère hydrophile.

2. Feuille d'enregistrement selon la revendication 1, dans laquelle le polymère cationique comprend une émulsion de polymère acrylique.

3. Feuille d'enregistrement selon la revendication 1 ou 2, dans laquelle le monomère hydrophile est un ester d'acide (méth)acrylique comportant un motif polyoxyalkylène.

4. Feuille d'enregistrement selon l'une quelconque des revendications 1 à 3, dans laquelle le polymère cationique est lié au polymère hydrophile ou réticulé avec le polymère hydrophile.

5. Feuille d'enregistrement selon l'une quelconque des revendications 1 à 4, dans laquelle le polymère cationique et le polymère hydrophile possèdent des groupes fonctionnels réactifs les uns avec les autres.

6. Feuille d'enregistrement selon l'une quelconque des revendications 1 à 5, dans laquelle le polymère cationique est un copolymère comprenant 0,1 à 50% en moles d'un monomère contenant un groupe amino tertiaire ou un groupe sel d'ammonium quaternaire et 0,1 à 25% en moles d'un monomère de réticulation contenant un groupe alcoxysilyle, dans laquelle le groupe amino tertiaire est susceptible d'être transformé en groupe sel d'amine tertiaire ou en groupe sel d'ammonium quaternaire dans le copolymère.
7. Feuille d'enregistrement selon l'une quelconque des revendications 1 à 6, dans laquelle la masse moléculaire moyenne en poids du polymère cationique est de  $0,2 \times 10^4$  à  $100 \times 10^4$ .
8. Feuille d'enregistrement selon l'une quelconque des revendications 1 à 7, dans laquelle la température de transition vitreuse du polymère cationique est de  $-20^\circ\text{C}$  à  $50^\circ\text{C}$ .
9. Feuille d'enregistrement selon l'une quelconque des revendications 1 à 8, dans laquelle le polymère hydrophile est au moins un élément choisi dans le groupe constitué par les dérivés de cellulose, les polymères de la série des alcools vinyliques, les polymères de la série des esters vinyliques et la polyvinylpyrrolidone.
10. Feuille d'enregistrement selon l'une quelconque des revendications 1 à 9, dans laquelle le polymère hydrophile est un polymère comportant au moins un groupe fonctionnel choisi dans le groupe constitué par un motif poly-oxyalkylène, un groupe acétoacétyle, un groupe carboxyle, un groupe anhydride d'acide et un groupe amino.
11. Feuille d'enregistrement selon l'une quelconque des revendications 1 à 10, dans laquelle le rapport du polymère cationique au polymère hydrophile est de 5/95 à 95/5 (premier/second, % en poids) sur la base des matières non volatiles.
12. Feuille d'enregistrement selon l'une quelconque des revendications 1 à 11, dans laquelle la couche absorbant l'encre contient par ailleurs un agent durcisseur.
13. Feuille d'enregistrement selon l'une quelconque des revendications 1 à 12, dans laquelle la couche absorbant l'encre contient par ailleurs un fixateur pour colorants.
14. Procédé de fabrication de la feuille d'enregistrement selon l'une quelconque des revendications 1 à 13 qui comprend le fait de former une couche absorbant l'encre sur au moins une face d'un substrat, dans lequel la couche absorbant l'encre a la composition de ladite couche absorbant l'encre de l'une quelconque des revendications 1-13.
15. Composition pour former une couche absorbant l'encre d'une feuille d'enregistrement, qui comprend:
  - une émulsion aqueuse de polymère cationique ayant un potentiel de surface (potentiel  $\zeta$ ) de 10 à 60 mV, dans laquelle le polymère cationique est un copolymère de monomères comprenant, soit
    - (1) un monomère cationique comportant des groupes sel d'amine tertiaire ou des groupes sel d'ammonium quaternaire et un monomère de réticulation comportant un groupe alcoxysilyle, soit
    - (2) un monomère cationique comportant des groupes sel amine tertiaire ou des groupes sel d'ammonium quaternaire, un monomère de réticulation comportant un groupe alcoxysilyle et un monomère hydrophile; et
  - un polymère hydrophile.